

PATENT SPECIFICATION

937,750

NO DRAWINGS.

937,750



Date of Application and filing Complete Specification :
Sept. 23, 1959. No. 32331/59.

Application made in United States of America (No. 762,951) on
Sept. 24, 1958.

Complete Specification Published : Sept. 25, 1963.

© Crown Copyright 1963.

Index at Acceptance :—Classes 1(2), AD41, AG12D41 ; and 1(1), A3B1.

International Classification :—C01g (B01j).

COMPLETE SPECIFICATION.

Metal Loading of Molecular Sieves.

We, UNION CARBIDE CORPORATION, of 270 Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America (assignee of Donald Wesley Breck and Robert Mitchell Milton), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing metal-loaded zeolitic molecular sieves which are suitable for use as catalysts, scavengers and getters.

The use of metals, as catalysts, scavengers, and getters in a number of chemical reactions and chemical systems is well known to the art. The effectiveness of the metal in such cases has been found to depend, to a considerable degree, on the form in which the metal is present in the reaction zone.

This invention comprises a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to absorb the oxygen molecule at the normal boiling point of oxygen which sieve contains at least 0.1 per cent iron, nickel, cobalt, copper, silver, gold, mercury, thallium, tin or lead or an oxide thereof in the inner adsorption region as hereinafter defined of said zeolitic molecular sieve.

The invention also comprises a process for preparing a zeolitic molecular sieve loaded with a metal which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to absorb the oxygen molecule at the normal boiling point of oxygen with an aqueous solution of a water-soluble

salt of iron, nickel, cobalt, copper, silver, gold, cadmium, zinc, mercury, thallium, tin, lead, whereby cations of the molecular sieve are exchanged for metal cations present in said aqueous solution, removing substantially all adsorbed water from the ion-exchanged molecular sieve, and intimately contacting the dehydrated, ion-exchanged molecular sieve with a reducing agent to reduce exchanged metal cations to elemental metal.

The resulting dehydrated molecular sieve loaded with the metal may be contacted with oxygen at elevated temperature to oxidise the metal.

Zeolitic molecular sieves, both natural and synthetic, are metal aluminosilicates. The crystalline structure of these materials is such that a relatively large adsorption area is present inside each crystal. Access to this area may be had by way of openings or pores in the crystal. Molecules are selectively adsorbed by molecular sieves on the basis of their size and polarity among other things.

By the phrase "inner adsorption region" as applied to the zeolitic molecular sieves of the present invention is meant that space within the crystal lattice to which access is had only through uniform sized pores of molecular dimensions.

Zeolitic molecular sieves consist basically of three-dimensional frameworks of SiO_2 and AlO_2 tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms. The electrovalence of the tetrahedra containing aluminium is balanced by the inclusion in the crystal of a cation, for example, an ion of an alkali metal, and alkaline earth metal, ammonia, amine complexes, or hydrogen. One cation may be exchanged for another by conventional ion-exchange techniques. The spaces between

the tetrahedra may be occupied by water or other adsorbate molecules.

The zeolites may be activated by driving off substantially all of the water of hydration. The space remaining in the crystals after activation is available for adsorption of adsorbate molecules. Any of this space not occupied by reduced elemental metal atoms will be available for adsorption of molecules having a size, shape, and energy of the molecular sieves.

The initial zeolite molecular sieves to be useful in the present invention, must be capable of adsorbing oxygen molecules at the normal boiling point of oxygen. Included among these are the natural zeolitic molecular sieves, chabazite, faujasite, erionite, mordenite, gmelinite, and the calcium form of analcite, and the synthetic zeolitic molecular sieves, zeolites A, D, L, R, S, T, X and Y. The natural materials are described in the mineralogical handbooks and texts. The characteristics of the synthetic materials and processes for making them are shown in the following Patents and Patent Applications.

Zeolite A is described and claimed in Patent No. 777,232.

Zeolite D is described and claimed in Patent Application No. 27153/58 (Serial No. 868,846).

Zeolite L is described and claimed in Patent Application No. 1501/59 (Serial No. 909,264).

Zeolite R is described and claimed in Patent Application No. 21151/58 (Serial No. 880,702).

Zeolite S is described and claimed in Patent Application No. 8316/59 (Serial No. 909,265).

Zeolite T is described and claimed in Patent Application No. 13933/59 (Serial No. 912,936).

Zeolite X is described and claimed in Patent No. 777,233.

Zeolite Y is described and claimed in Patent Application No. 11328/59 (Serial No. 909,266).

In accordance with the process of the present invention, a zeolitic molecular sieve capable of adsorbing a substantial amount of oxygen at the normal boiling point of oxygen is ion exchanged by contacting the molecular sieve with an aqueous solution of a water-soluble salt of the metal to be reduced to the elemental state. When sufficient ion exchange occurs, the exchange zeolite is removed from contact with the exchanging solution and heated for example to a temperature of about 350° C. in a flowing stream of inert, dry gas or in a vacuum. The activated molecular sieve is then ready for reduction of the cations to the elemental metal. It has been found that the most satisfactory dispersion of the

elemental metal throughout the adsorption region of the zeolitic molecular sieves is obtained if substantially all of the water is removed from the molecular sieves prior to the reduction step. When the molecular sieves are only partially dehydrated, the products are still usable, but will not have the metal as well dispersed, thereby reducing the specific surface of the metal in the molecular sieves with a corresponding reduction in the surface activity of the contained metal.

The activated molecular sieve is then treated with a reducing agent. Alkali metal vapors or preferably gaseous hydrogen, are suitable reducing agents for the process of the present invention. The reduction may be accomplished by passing the gaseous or vaporous reducing agent through a bed of the ion-exchanged, activated zeolitic molecular sieves. In the case of the alkali metals, it is sufficient to mix the molten metals with the ion-exchanged activated zeolite; sufficient vapors are given off by the molten metal to effect the reduction.

The reduction should be effected in an inert atmosphere as should be the subsequent cooling of the material. The maximum temperature of reduction must be below the temperature at which the crystal structure of the zeolitic molecular sieve is destroyed, i.e. 650° C. or preferably 500° C.

The metals which may be loaded into the zeolitic molecular sieves by the present process are copper, silver, gold, zinc, cadmium, mercury, thallium, tin, lead, iron, cobalt, and nickel.

EXAMPLE I.

Zeolite X (100 grams) was placed in a 16-millimeter inside diameter glass column to a bed depth of 70 centimeters. A 0.22 molar nickel nitrate solution (128 grams $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 2 liters water) was passed up through the column at a rate of 10 milliliters per minute. The zeolite was washed after completion of exchange by passing 500 milliliters distilled water through the column. The zeolite was then removed from the column and dried at 100° C. X-ray diffraction analysis showed the crystal structure of the zeolite to be intact.

The nickel-exchanged zeolite was placed in a vertical tube and heated under a hydrogen purge of 0.5 cubic feet per hour at 300–350° C. for three hours until dehydrated. The temperature was then increased to 500° C. for three hours while still under hydrogen purge to accomplish hydrogen reduction of the nickel-exchanged zeolite. The zeolite was then cooled overnight under 5 psig hydrogen. The product was uniformly black and X-ray diffraction analysis of the zeolite indicated the presence

of elemental nickel. Chemical analysis of the product indicated 8.6 weight per cent nickel.

EXAMPLE II.

5 Zeolite X powder (314 grams) was slurried at room temperature with two liters of 0.2 molar silver nitrate (containing 68 grams AgNO_3). After the exchange reaction was complete, the zeolite was washed with water until the wash effluent was free of silver-ions. The zeolite was then dried at 110° C. Chemical analysis of the zeolite indicated the presence of 11.3 per cent silver.

15 The silver-exchanged zeolite X was heated in a nitrogen purge at 350° C. for 2 hours. After cooling the zeolite to 200° C., hydrogen was admitted at about 1 cubic foot per hour and the heating continued for one hour. The white silver-exchanged zeolite X turned black in the presence of hydrogen. An exposure of the silver-loaded zeolite X to air, after reduction, changed the color from black to yellow-brown. X-ray diffraction analysis of the product after reduction showed the crystal structure to be intact and the elemental silver present had a particle size of less than 10^{-6} centimeters.

EXAMPLE III.

30 A solution of mercuric nitrate was prepared by dissolving 90 grams of $\text{Hg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in one liter of water. About 6 grams of NaNO_3 was added to a buffering agent and concentrated acetic acid was added until the solution was clear.

35 Zeolite X powder (100 grams) was slowly added to the above solution and then allowed to stand for 1½ hours. The zeolite was then filtered, washed and dried at 100° C. for two hours.

40 The mercury-exchanged zeolite containing 57.4 weight per cent mercury was placed in a horizontal tube furnace and heated under a hydrogen purge of 5 cubic feet per hour. The bed was heated at 100° C. for 1½ hours and then allowed to cool overnight. The bed was then heated at 110—200° C. for 1½ hours, then at 200—220° C. for five hours, all under a hydrogen purge of 5 cubic feet per hour. The bed was cooled overnight and then heated at 200—350° C. for 2½ hours under a hydrogen purge of 5 cubic feet per hour and allowed to cool to room temperature. The bed color changed from yellow to gray during the action. Even though an appreciable amount of mercury was distilled out of the zeolite, the zeolite product contained 2.5 weight per cent mercury.

EXAMPLE IV.

A solution of cadmium nitrate was prepared by dissolving 80 grams of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in one liter of distilled water. This solution was mixed with 100 grams of zeolite X and allowed to stand for 2½ hours. The zeolite was then filtered and dried at 100° C. for two hours.

65 The cadmium-exchanged zeolite containing 177.9 weight per cent cadmium was placed in a horizontal tube furnace and heated at 90—230° C. for two hours under 2—3 cubic feet per hour hydrogen. The bed color changed from white to yellow. Chemical analysis of the zeolite product indicated that it contained 16.6 weight per cent cadmium. On further heating at temperatures up to 550° C. for 5½ hours some of the cadmium metal was distilled out. The zeolite color turned to white, and the cadmium content dropped to 14.8 per cent.

EXAMPLE V.

85 A solution of lead nitrate was prepared by dissolving 86 grams of $\text{Pb}(\text{NO}_3)_2$ in one liter of distilled water. This solution was then slurried with 100 grams of zeolite X for one hour. The zeolite was then filtered and dried at 100° C. Chemical analysis indicated that the lead-exchanged zeolite X contained 31.4 weight per cent lead.

90 The lead-exchanged zeolite was placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 110—360° C. for 1½ hours and at 200—475° C. for seven hours. The bed color changed from white to black. Chemical analysis of the product indicated that it contained 36.4 weight per cent lead. X-ray diffraction analysis of the product showed that the crystal structure was intact and elemental lead was present.

EXAMPLE VI.

105 A solution of copper nitrate was prepared by dissolving 12.1 grams $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in one liter of distilled water. This solution was mixed with 100 grams of zeolite X and allowed to stand for ten minutes. The zeolite was filtered and dried overnight at 100° C.

110 The copper-exchanged zeolite containing 3.0 weight per cent copper was placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 100—265° C. for eight hours and then at 235—450° C. for four hours. The bed color changed from light blue to pink-rose. Chemical analysis of the dried product indicated 3.5 weight per cent copper. X-ray diffraction analysis of the product showed no crystallographic decomposition.

EXAMPLE VII.

A solution of iron nitrate was prepared by dissolving 20.2 grams $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in one liter distilled water. This solution

was slurried with 100 grams zeolite X and allowed to stand for ten minutes. The zeolite was filtered and dried at 100° C. for three hours.

- 5 This iron-exchanged zeolite containing 2.4 weight per cent iron was then placed in a horizontal tube furnace and heated under 2 cubic feet per hour hydrogen at 100—320° C. for ten hours. The bed color
10 changed from yellow-brown to gray-brown. Chemical analysis of the product indicated 3.2 weight per cent iron. X-ray diffraction analysis of the product showed no crystallographic decomposition.

15 **EXAMPLE VIII.**

- Zeolite A powder (80 grams) was slurried at room temperature into 860 milliliters of 0.2 M silver nitrate solution (contained 28.2 grams AgNO_3). The mixture was allowed
20 to stand about $\frac{1}{2}$ hour and was then filtered. The solid was then washed with water until free of silver. The solid was then dried at 100° C.

- The silver-exchanged zeolite A containing 19.9 weight per cent silver was placed in horizontal tube furnace and dehydrated by heating at 350—400° C. for 1 $\frac{1}{2}$ hours. The zeolite was then cooled to room temperature. Hydrogen (0.5 cubic feet per hour) was passed through the bed for 20 minutes. The bed turned yellow-brown. The zeolite was heated to 100—200° C. while passing hydrogen through it for 25 minutes. The product had a uniformly
30 dark brown color and contained 23.5 weight per cent silver. X-ray diffraction analysis of the silver A zeolite after reduction indicated that hydrogen exchange had occurred and that elemental silver was present.

40 **EXAMPLE IX.**

- A sample of mordenite (in the form of beach pebbles found in Nova Scotia) with an approximate composition of $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ where R is $(\text{Na} +)_2$ and $\text{Ca} + +$ was ground to pass through a 150 U.S. Standard mesh screen. A 7.6 gram portion of this powder was mixed with 150 milliliters aqueous solution containing 1.5 grams of silver nitrate. This mixture was
45 allowed to stand with frequent agitation for 1 $\frac{1}{2}$ hours. It was then filtered and washed with water until the filtrate gave a negative test for silver ion. The zeolite was dried at 110° C.

- 55 The silver-exchanged mordenite was placed in a horizontal tube furnace and heated at 350° C. for 3 hours in a stream of hydrogen gas. Chemical analysis of the product indicated that it contained 9.3 weight per cent silver. The structure of the
60 crystal was indicated by X-ray diffraction techniques to be a hydrogen-exchanged form of mordenite.

EXAMPLE X.

A quantity (15 grams) of sodium zeolite X powder was put into 50 milliliters of an aqueous solution of thallous sulphate (18 grams per liter of solution) and the suspension was stirred for 20 minutes. The zeolite powder was filtered from the solution and washed with distilled water. The washed zeolite was then dehydrated by heating to 375° C. under reduced pressure. A few grams of the activated, thallous-exchanged, zeolite powder were mixed with a few grams of metallic sodium in a 250 ml. flask and heated to a temperature in the range of 150° C. to 180° C. with continuous stirring under an argon atmosphere. The final product was black in color and contained 31 weight per cent of thallium. The presence of thallium metal was confirmed by X-ray.

The processes illustrated by Examples I to X can be employed to make a metal-containing zeolitic molecular sieve only when a suitable stable cation of the metal to be introduced into the molecular sieve is available. This requirement cannot always be met. For example, platinum occurs in simple ionic salts in the anionic part of the salt. Thus the usual cation-exchange techniques for introducing platinum into the crystal structure of a zeolite molecular sieve cannot be employed. In some instances, notably with chromium ions, the simple cation is not stable except in acidic solutions which destroy the crystal structure of the zeolitic molecular sieve.

In the previous examples, the reducing agents are oxidized to cations which take up the position in the zeolitic molecular sieve structure formerly occupied by the cation which was reduced. However, it has been found that zeolitic molecular sieve cations may be reduced by reducing agents which are not oxidized to cations even though there are no obvious cations to replace them. This may be illustrated by the following examples.

EXAMPLE XI.

Hydrated Cu(II) X zeolite (15 grams) containing 12.2 weight per cent Cu on an anhydrous basis was placed in a 1 inch "Pyrex" tube ("Pyrex" is a Registered Trade Mark). The tube was controlled at 375° C. in a split tube furnace for 2 $\frac{1}{2}$ hours in a stream of nitrogen. The tube was then cooled to 350° C. and a stream of carbon monoxide was continued for 2 $\frac{1}{2}$ hours during which time the zeolite changed from light blue to light purple. The tube was then cooled to 350° C. and a stream of carbon monoxide was continued for 2 $\frac{1}{2}$ hours during which time the zeolite changed from light blue to light purple. This color change is indicative of reduction. The

sample was cooled in nitrogen. It was removed and submitted for analysis without exposure to air. The analysis showed 9.4 weight per cent copper metal on an anhydrous basis.

A sample of the same starting zeolite was treated under identical conditions of temperature and time with hydrogen instead of carbon monoxide. The reduction took place much more rapidly than with carbon monoxide. Analysis of this sample showed 9.8 weight per cent copper metal on an anhydrous basis.

In this case, it is believed that hydrogen ions were obtained from residual water remaining in the zeolitic molecular sieve after the activation step.

EXAMPLE XII.

Hydrated Cu(II) X zeolite (25 grams) containing 12.2 weight per cent Cu on an activated basis was suspended in 200 ml. distilled water in a 500 ml. 3-necked flask fitted with a condenser, a thermometer, and a stirrer. An inert atmosphere was maintained over the suspension. Hydrazine hydrochloride (5.25 grams, .05 moles) was added to the suspension. A solution of sodium hydroxide (4.0 grams, .1 moles) was added dropwise over a period of 30 minutes. Copious amounts of gas, presumably nitrogen, were evolved. The zeolite first turned colorless, probably forming the copper (I) X zeolite, and then deep red brown. The mixture was heated to 100° C. to ensure complete reaction and destruction of excess hydrazine. The zeolite was filtered and washed with water and acetone under an inert atmosphere. It was extremely reactive in air, turning light blue in a few minutes. A sample was heated to 350° C. in vacuo for 2½ hours. No visible change occurred. Analysis showed 8.1 weight per cent copper metal on an anhydrous basis and less than 0.1 per cent nitrogen.

It is a simple matter to obtain metal oxide-loaded molecular sieves from the metal-loaded molecular sieves by standard oxidation procedures. Exposure of the metal-loaded molecular sieve to oxygen at an elevated temperature is quite satisfactory. However, the temperature should not exceed the temperature at which the crystal structure of the zeolitic molecular sieve will be destroyed.

The maximum metal that may be incorporated in the zeolitic molecular sieves by the process of the present invention is limited by the extent to which the molecular sieves may be ion-exchanged with the desired cations. However since the metals are distributed throughout the molecular sieves according to the location of the ion-exchange site of the crystals, it is possible

to obtain a high degree of dispersion of the metal throughout the crystals and the contained metal has a very high specific surface.

The products produced by the process of the present invention are quite useful as catalysts, and particularly as selective catalysts for the specific catalysis of reactants which are mixed with other materials which are not adsorbed by the zeolitic molecular sieve. The adsorbed materials react leaving the non-adsorbed materials unreacted.

Similarly, the products are useful as selective getters, gettering certain components of a mixture without affecting the other components.

The metal-containing zeolite molecular sieves are useful as a means for effecting the controlled addition of metals to reaction systems.

Still another advantage of the use of metal-loaded zeolite molecular sieves resides in the fact that the tendency for the metal to migrate is minimized. Normal catalysts consisting of supported metals exhibit migration of the metal during catalysis thereby giving rise to unequal distribution of catalyst material with a corresponding decrease in catalytic effectiveness.

As used herein the term "activation" is employed to designate the removal of water from the zeolitic molecular sieves, i.e. dehydration, and does not refer to catalytic activity. The zeolitic molecular sieves containing the elemental metal exhibit catalytic activity.

The process of the present invention provides materials having surface areas about four times that expected with most alumina, silica or aluminosilicate supported metals thereby providing a greater surface area available for reaction. Since the external surface of the molecular sieve represents less than 1 per cent of the total surface area it may be seen that there is an extremely large area available for chemisorption and catalysis in the internal portion of the molecular sieve. Since this region is available only through pores of molecular size it may be seen that selective chemisorption and catalysis may be obtained in a system containing a mixture of molecules some of which are too large to enter the pores whereas others are capable of entering the pores.

Co-pending Application No. 32330/59 (Serial No. 937,749) discloses and claims a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains platinum, aluminum, chromium, molybdenum, tungsten, manganese, rhenium, titanium, zirconium, hafnium, vanadium, iron, cobalt, nickel, copper or oxides of these metals in

the inner adsorption region (as therein defined) of said zeolitic molecular sieve.

Co-pending Application No. 32330/59 (Serial No. 937,749) also discloses and claims a process for preparing a zeolitic molecular sieve loaded with a metal or oxide thereof, comprising contacting a dehydrated molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule (as therein defined) with a fluid, decomposable compound of copper, silver, gold, platinum, iridium, osmium, palladium, rhodium, ruthenium, zinc, cadmium, aluminum, tin, lead, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, titanium, zirconium, hafnium or vanadium, whereby said decomposable compound is adsorbed into the inner adsorption region (as therein defined) of said molecular sieve and decomposing said decomposable compound to the elemental metal.

Co-pending Application No. 32329/59 (Serial No. 937,748) discloses and claims a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains at least 0.1% by weight of gold, iridium, osmium, palladium, rhodium, or ruthenium or an oxide thereof in the inner adsorption region (as therein defined) of said zeolitic molecular sieve.

Co-pending Application No. 32329/59 (Serial No. 937,748) also discloses and claims a process for producing a zeolitic molecular sieve loaded with a metal or oxide thereof which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule with an aqueous solution of a complex cation comprising an amine or ammonia and copper, silver, gold, chromium, zinc, cadmium, tin, lead, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, or platinum, whereby cations of the molecular sieve are exchanged for said complex cations, removing substantially all the adsorbed water from the ion-exchanged molecular sieve in an inert atmosphere, and reducing said complex cations in said dehydrated molecular sieve to the elemental metal.

We make no claim to a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains iron, nickel, cobalt, copper or oxides of these metals in the inner adsorption region as claimed in co-pending Application No. 32330/59 (Serial No. 937,749).

We also make no claim to a dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the benzene molecule, which sieve contains gold, or an oxide thereof in the inner adsorption region as claimed in co-pending Application No. 32329/59 (Serial No. 937,748).

Subject to the foregoing disclaimers,
WHAT WE CLAIM IS:—

1. A dehydrated zeolitic molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the oxygen molecule at the normal boiling point of oxygen which sieve contains iron, nickel, cobalt, copper, silver, gold, mercury, thallium, tin or lead or an oxide thereof in the inner adsorption region as hereinbefore defined of said zeolitic molecular sieve.

2. A dehydrated molecular sieve as claimed in Claim 1 substantially as hereinbefore described with reference to and as illustrated in the examples.

3. A process for preparing a zeolitic molecular sieve loaded with a metal which comprises contacting a molecular sieve having uniform sized pores at least large enough in cross-sectional area to admit the oxygen molecule at the normal boiling point of oxygen with an aqueous solution of a water-soluble salt of iron, nickel, cobalt, copper, silver, gold, cadmium, zinc, mercury, thallium, tin, lead, whereby cations of the molecular sieve are exchanged for metal cations present in said aqueous solution, and intimately contacting the dehydrated, ion-exchanged molecular sieve with a reducing agent to reduce exchanged metal cations to elemental metal.

4. A process as claimed in Claim 3 in which the ion-exchanged molecular sieve is dehydrated prior to contact with the reducing agent.

5. A process as claimed in Claim 3 in which the exchange metal cation is reduced to elemental metal by contacting the ion-exchanged molecular sieve with a reducing agent in an aqueous layer.

6. A process as claimed in any of Claims 3 to 5 in which the zeolitic molecular sieve loaded with copper, silver, gold, mercury, thallium, tin, lead, iron, nickel, cobalt, cadmium or zinc is contacted with oxygen atoms at elevated temperature to oxidize the metal.

7. A process as claimed in Claim 3 for preparing a zeolitic molecular sieve loaded with a metal substantially as hereinbefore described with reference to and as illustrated in any of the examples.

8. A dehydrated zeolitic molecular sieve loaded with a metal when prepared by the process as claimed in any of Claims 3 to 7.

W. P. THOMPSON & CO.,
12 Church Street,
Liverpool 1,
Chartered Patent Agents.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.



11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
2212
2213
2214
2215
2216
2217
2218
2219
2220
2221
2222
2223
2224
2225
2226
2227
2228
2229
2230
2231
2232
2233
2234
2235
2236
2237